PREPARATION OF BIODIESEL FROM WASTE COOKING OIL USING SINGLE STEP BATCH CATALYST WITH THE AID OF KOH AS A CATALYST

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Tarikh :16 MAY 2008

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FACULTY OF CHEMICAL ENGINEERING

UNIVERSITI MALAYSIA PAHANG

"I declare that this thesis is the result of my own research except as cited references. The thesis has not been accepted for any degree and is concurrently submitted in candidature of any degree"

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Name of Candidate	: NAJWA BINTI MOHD NOR
Date	:16 MAY 2008

DEDICATION

Special dedication to my beloved father, mother, brothers and sisters………………..

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Wassalam

ABSTRACT

Biodiesel is a cleaner burning diesel replacement fuel processed from natural, renewable derived from biological sources such as used vegetable oils and animal fats. The type of process that used to produce biodiesel is transesterification. Transesterification is the commonly process that used widely compare to other process. This process is important to convert free fatty acid (FFA) in oil to ester. In this research, waste cooking oil is used as raw material with Potassium hydroxide (KOH) as catalyst and methanol as a solvent. The reaction has been done in a water bath. The parameter that been investigated were reaction time and catalyst concentration while reaction temperature was fixed at 65˚C. Finally, the biodiesel sample was tested on several parameters which are the yield, thin layer chromatography (TLC), and moisture content. The analysis has been done using Response Surface Methodology (RSM) to find the optimum condition based on higher yield and TLC. It is to ensure its meet the standard requirement of ASTM D6751 for biodiesel B100. The optimum result for higher yield is 73.38 minute reaction time and using 1.33% catalyst concentration and the optimum result for higher TLC is 90 minute reaction time and 0.5% catalyst concentration.

ABSTRAK

Biodiesel adalah pengganti minyak pembakar diesel yang bersih yang diproses dari alam semulajadi, ia dapat diperbaharui hasil daripada sumber biologis seperti minyak sayuran dan lemak haiwan. Proses yang digunakan untuk menghasilkan biodiesel adalah *transesterification*. *Transesterification* adalah proses yang selalu digunakan secara meluas berbanding proses yang lain. Proses ini penting untuk merubah asid lemak berlebihan ke minyak atau ester. Dalam eksperimen ini, minyak masak yang telah digunakan dijadikan bahan mentah dan *Potassium hydroxide (KOH)* sebagai mangkin dan methanol untuk pelarut. Tindak balas ini telah dijalankan menggunakan *water bath*. Parameter yang harus dikaji adalah masa tindakbalas dan kepekatan mangkin, manakala suhu tindakbalas ditetapkan pada 65˚C. Akhirnya, sampel biodiesel akan diuji ke atas beberapa parameter iaitu jumlah hasil, kepingan nipis kromatografi (TLC), dan kandungan air. Analisisnya pula menggunakan perisian komputer Response Surface Methhodology (RSM) untuk mencari keadaan optimum berdasarkan jumlah hasil dan TLC yang tinggi. Ini untuk memastikan hasil mencapai norma piawaian ASTM D6751 untuk biodiesel B100. Data optimum untuk mencapai hasil biodiesel tertinggi adalah 73.38 minit masa tindak balas dan 1.33% kepekatan mangkin dan data optimum untuk mencapai TLC tertinggi adalah 90 minit masa tindak balas dan 0.5% kepekatan mangkin.

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LIST OF ABBREVIATIONS

^{0}C	Degree Celcius
ANOVA	analysis of variance
CCD	Central Composite Design
DOE	Design of Experiment
FFA	free fatty acid
h	hour
KOH	Potassium Hydroxide
Min	minute
ml	mililiter
NaOH	Sodium Hydroxide
RSM	Response Surface Methodology
TLC	Thin Layer Chromatography

CHAPTER 1

INTRODUCTION

1.1 Introduction

As world's petroleum supplies are becoming constrained, attention has been directed to find out alternative sources of fuels for engines. The non-renewable nature and limited resources of petroleum fuels have become a matter of great concern. After the 1973 oil embargo, it had been very important to study the alternative sources of fuel for diesel engine because of the concern over the availability and the price of petroleum based fuels. The present reservation of fuels used in internal combustion (IC) engines including diesel will deplete within 40 years if consumed at an increasing rate estimated to be of the order of 3% per annum. All these aspects have drawn the attention to conserve and stretch the oil reserves by way of alternative fuel research.

Thus, the use of alternatives energy such as hybrid technology and hydrogen cell requires extra modification to the vehicle engine. As a result, higher costs, longer duration of time to develop were needed to upgrade this technology. Thus, research on new energy sources, such as biodiesel has become more importance in recent years.

1.2 Background Of Study

Biodiesel is the alternative fuel substance that will replace the petrol one day. It can be commercialize because it has more advantages compare to other source of fuel. Only the little fossil energy is required to move biodiesel. Special pumps or high pressure equipment for fuelling are not needed for this specification. In addition, it can be used in conventional diesel engine, so we do not need any upgrading or new purchasing for our engine.

In petrol, the scientists believe carbon dioxide is one of the main greenhouse gases contributing to global warming. The 100% biodiesel will reduces carbon dioxide emissions by more than 75% over petroleum diesel. If we use a blend of 20% biodiesel, it will reduce carbon dioxide emission by 15%. Biodiesel also produces less particulate matter, carbon monoxide, and sulphur dioxide emission which is all air pollutants under the Clean Air Act.

This renewable fuel can directly replace petroleum product since it can be used in conventional diesel engines. The biodiesel also can reduce the country's dependence on imported oil. Biodiesel offers safety benefits compare petroleum diesel because it is much less combustible, with a flash point greater than 150°C, compares to 77°C for petroleum diesel.

The energy that release for biodiesel is about same for petroleum diesel (118,000 vs. 130,500BTUs). Therefore, engine torque and horse power remain virtually same. Biodiesel is safer than petroleum diesel to handle or store. Biodiesel does not produce dangerous vapors at normal ambient temperatures or room temperatures, and it can be stored in the same containers and tank as petroleum diesel.

The disadvantages of biodiesel is based on the sources that used to produced the biodiesel, as an example if we produce biodiesel from waste cooking oil, the process will also produce FFA (free fatty acid) as a side product. This biodiesel production to commercialize is still along with the research to cover the disadvantages.

The biodiesel used has grown dramatically during the last few years. The Energy Policy Act was amended by the Energy Conservation Reauthorization Act of 1998 to include biodiesel fuel use as a way for federal, state, and public utility fleets to meet requirements for using alternative fuels. In Malaysia there are plenty company that starting this biodiesel production using Jarak fruit or the scientific name is Jathopra curcas Linn, but during the production it still come along with research with our local university like Universiti Malaysia Pahang (UMP).

1.3 Problem Statement

In Malaysia, government have gives subsidized to petroleum oil in transportation sector. It shows that petroleum price is in unstable economy. Thus, using waste cooking oil will make the biodiesel price is compatible than subsidized petroleum diesel. The availability of raw material and cheaper cost are the main criteria for choosing good raw material.

The high contain of fatty acid need to be synthesize using single step of catalyzed process to prevent the high yield of soap. The single step is more economical process compare to other process. The transesterification process is used because its give high yield in reaction, reduce the production cost and low reaction time rate. In the transesterification process, methanol will be use as alcohol solvent because its cheaper compares other alcohol solvent.

1.4 Objective

The main purpose of this research is to produce biodiesel from waste cooking oil via single step batch catalyzed process and to find optimum condition using DOE software to get higher yield and thin layer chromatography (TLC).

1.5 Scope Of Researchs

This research aim is a study in production of biodiesel using waste cooking oil as the feedstock. To obtain the research objective, three elements have been identified to be studied in this experiment. The three elements are:

i. To study the effect of reaction time and catalyst concentration. In the transesterification process.
ii. To analyze several parameter such as yield, TLC and moisture content.
iii. To study single step catalyzed transesterification process.’

CHAPTER 2

LITERATURE REVIEW

2.1.1 Biodiesel Properties

Biodiesel is other alternative fuel to replace petrol diesel that is produces by chemically reacting a vegetables oil or animal fat. There are many benefits we get from biodiesel in comparison to petroleum based fuels. It includes, the reduction of CO emission by approximately 50% and carbon dioxide by 78% on a net lifecycle basis. It happens because the carbon in biodiesel emissions is recycled from carbon that was in the atmosphere, rather than the carbon introduced from petroleum that was sequestered in the earth's crust. [Sheehan, 1998]. Biodiesel also contains fewer aromatic hydrocarbons and biodiesel has a higher cetane rating than petrodiesel, which can improve performance and clean up emissions compared to crude petrodiesel.

The most important fact is biodiesel is biodegradable and non-toxic. The U.S. Department of Energy confirms that biodiesel is less toxic than table salt and biodegrades as quickly as sugar. In the United States, biodiesel is the only alternative fuel to have successfully completed the Health Effects Testing requirements (Tier I and Tier II) of the Clean Air Act (1990). The other advantages of biodiesel are, when biodiesel were used in a blend with petroleum diesel, there are fewer formal studies about the effects on pure biodiesel in unmodified engines and vehicles in day to day use. Fuel meeting the standards and engine parts that can withstand the greater solvent properties of biodiesel is expected to run without any additional problems than the use of petroleum diesel.

Properties	Biodiesel (vegetable oil methyl ester)					
	Peanut	Soyabean	Palm	Sunflower	Linseed	Tallow
Kinematic viscosity at 37.8 1˚C(m^2/s)	4.9	4.5	5.7	4.6	3.59	-
Cetane number(˚C)	54	45	62	49	52	-
Lower heating value (MJ/l)	33.6	33.5	33.5	33.5	35.3	-
Cloud point(˚C)	5	1	13	1	-	12
Pour point(˚C)	-	-7	-	-	-15	9
Flash point(˚C)	176	178	164	183	172	96
Density(g/ml)	0.883	0.885	0.88	0.86	0.874	-
Carbon residue (wt%)	-	1.74	-	-	1.83	-

Table 2.1 Properties of Biodiesel

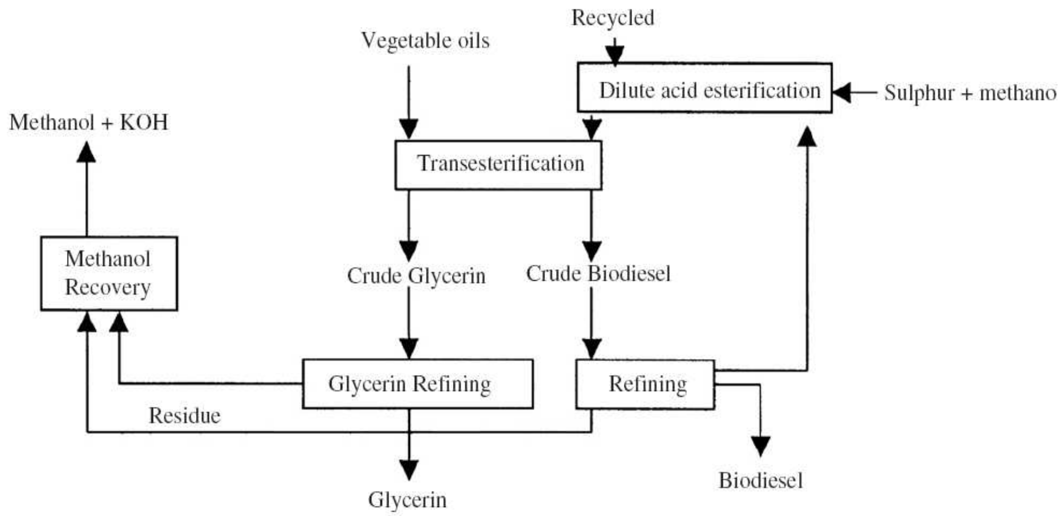

Figure 2.2 A scheme of the flow chart

The characteristics of biodiesel are close to diesel fuels, and therefore biodiesel becomes a strong candidate to replace the diesel fuels if the need arises. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-third that of the triglyceride, reduces the viscosity by a factor of about eight and increases the volatility marginally. Biodiesel has viscosity close to diesel fuels. These esters contain 10 to 11% oxygen by weight, which may encourage more combustion than hydrocarbon-based diesel fuels in an engine. The cetane number of biodiesel is around 50. The use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the finished diesel fuel without having any negative effect on its cold flow properties. Since the volatility increases marginally, the starting problem persists in cold conditions. Biodiesel has lower volumetric heating values (about 12%) than diesel fuels but has a high cetane number and flash point. The esters have cloud point and pour points that are 15 to 258C higher than those of diesel fuels.

2.1.2 Raw Materials

The limitation of available sources for petroleum exploration is a strong motivation to focus on renewable energy. There are few categorize for raw materials to produce biodiesel which is animal fat, vegetable oil and waste cooking oil. Each raw material have advantages and disadvantages.

2.1.2.1 Animal Fat

The fact that is biodiesel can produced from 100 percent animal fats and fulfills the current EN 14214 for fatty acid methyl esters, as long as state-of-the-art process technology is applied.When chemical properties of various feedstock materials for biodiesel production are compared, the main difference between vegetable oils like rapeseed oil and animal fats can be found in the diverse fatty acid composition. While rapeseed oil and soybean oil have a high content of unsaturated fatty acids, mainly oleic acid and linoleic acid, animal fats like tallow or lard have a major content of saturated fatty acids (e.g., palmitic and stearic acid). The increased amount of saturated fatty acids shows a reversed trend for two main fuelproperties. While the oxidationstability of biodiesel derived from animal fats increases, the cold temperature performance decreases with a rising content of saturated fatty acids. Figure 1 shows the dependence of the content of saturated fatty acids in biodiesel – without additives – on its cold filter plugging point (CFPP).

2.1.2.2 Vegetable Oil

Vegetable oil can be divided into two categories, virgin oil and waste vegetable oil. Virgin oil feedstock, rapeseed and soybean oils are most commonly used, soybean oil alone accounting for about ninety percent of all fuel stocks; It also can be obtained from field pennycress and Jatropha other crops such as mustard, flax, sunflower, canola, palm oil, hemp, jatropha, and even algae show promise. The other one is waste vegetable oil (WVO). The advantages of using vegetable oils as fuels are it do not over burden the environment with emissions, vegetable oil's production requires lesser energy input in production, and simpler processing technology. While the disadvantages of vegetable oil are these are not economically feasible yet and it still need further R&D work for development of on farm processing technology. Many advocates suggest that waste vegetable oil is the best source of oil to produce biodiesel.

2.1.2.3 Waste Cooking Oil

Waste cooking oil is purified from fat of plant or animal origin, which is liquid at room temperature. Proper disposal of used cooking oil is an important waste-management concern. Oil is lighter than water and tends to spread into thin and broad membranes which hinder the oxygenation of water. Because of this a single litre of oil can contaminate as much as 1 million liters of water. Also, oil can congeal on pipes provoking blockages, because of this, cooking oil should never be dumped on the kitchen sing or in the toilet bowl. The proper way to dispose it is to put it in a sealed non-recyclable container and discard it with regular garbage. Better yet, cooking oil can be recycled. It can be used to produce soap and biodiesel.

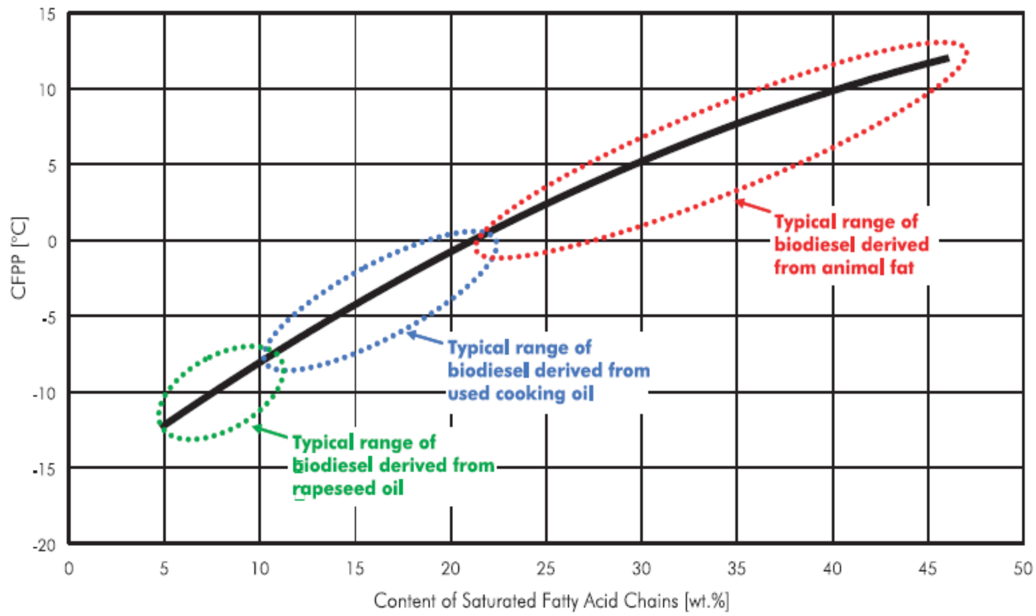

Figure 2.1 Content of Saturated Fatty Acid Chains

2.2 Process

2.2.1 Pyrolisis

Pyrolysis is the conversion of one substance into another by means of heat or by heat in presence of a catalyst. The paralysed material can be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum. Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engine. Thermal decomposition of triglycerides produces alkanes, alkenes, alkadines, aromatics and carboxylic acids [Ma *et al*, 1990]

2.2.2 Micro Emulsion

The problem of the high viscosity of vegetable oils can be solving by emulsification with solvents such as methanol, ethanol and 1-butanol. An emulsification is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1–150 nm range, formed spontaneously from two normally immiscible liquids. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. Short term performance of micro-emulsions of aqueous ethanol in soybean oil was nearly as good as that of no. 2 diesel, in spite of the lower cetane number and energy content [Srivastava *et al*, 2000]

2.2.3 Transesterification

Transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol. The reactions are often catalyzed by an acid or a base. Transesterification is crucial for producing biodiesel from biolipids. Transesterification is the process triglycerides react with an alcohol, generally methanol or ethanol to produce esters and glycerine [Miguel *et al.*, 2001]. A catalyst is added to the reaction to make it possible. The catalyst is usually used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is required to shift the equilibrium to the product side. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol [Ma *et al*, 1990]. Alkali-catalyzed transesterification is much faster than acid catalyzed transesterification and is most often used commercially [Ma *et al*, 1990].

$$
\begin{array}{lcccccc}
CH_2\text{-}OOC\text{-}R_1 & & & & R_1\text{-}COO\text{-}R' & & CH_2\text{-}OH \\
| & & & \text{Catalyst} & & & | \\
CH\text{-}OOC\text{-}R_2 & + & 3R'OH & \leftrightarrow & R_2\text{-}COO\text{-}R' & + & CH\text{-}OH \\
| & & & & & & | \\
CH_2\text{-}OOC\text{-}R_3 & & & & R_3\text{-}COO\text{-}R' & & CH_2\text{-}OH \\
& & & & & & \\
\text{Glycerides} & & \text{Alcohol} & & \text{Esters} & & \text{Glycerin}
\end{array}
$$

$$\text{Triglycerides (TG)} + \mathrm{R'OH} \underset{k_2}{\overset{k_1}{\leftrightarrow}} \text{Diglycerides (DG)} + \mathrm{R'COOR_1},$$

$$\text{Diglycerides (DG)} + \mathrm{R'OH} \underset{k_4}{\overset{k_3}{\leftrightarrow}} \text{Monoglycerides (MG)} + \mathrm{R'COOR_2},$$

$$\text{Monoglycerides (MG)} + \mathrm{R'OH} \underset{k_6}{\overset{k_5}{\leftrightarrow}} \text{Glycerin (GL)} + \mathrm{R'COOR_3}.$$

Figure 2.2 Transesterification Process

R1, R2, R3, R’ represent various alkyl group. The process of transesterification brings about drastic change in viscosity of vegetable oil. The biodiesel thus produced by this process is totally miscible with mineral diesel in any proportion. Biodiesel viscosity comes very close to that of mineral diesel hence no problems in the existing fuel handling system. Flash point of the biodiesel gets lowered after esterification and the cetane number gets improved. Even lower concentrations of biodiesel act as cetane number improver for biodiesel blend. Calorific value of biodiesel is also found to be very close to mineral diesel [Agarwal, 2001].

Diesel engine can perform satisfactory for long run on biodiesel without any hardware modifications. Twenty percent biodiesel is the optimum concentration for biodiesel blend with improved performance. Increase in exhaust temperature however lead to increased NOx emissions from the engine. While short-term tests are almost positive, long-term use of neat vegetable oils or their blend with diesel leads to various engine problems such as, injector coking, ring sticking, injector deposits etc. [Muniyappa *et al*., 1996]. High viscosity, low volatility and a tendency for polymerization in the cylinder are root causes of many problems associated with direct use of these oils as fuels.